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FEASIBILITY DEMONSTRATION OF EXCIPLEX FLUORESCENCE MEASUREMENTS IN EVAPORATING LAMINAR SPRAYS OF DIESEL FUEL

Final Technical Report Grant: FA9550-10-1-0077

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May 15, 2011

SUMMARY/OVERVIEW

A six-month seed project was funded to investigate the feasibility of applying quantitatively laser diagnostic techniques to jet fuel surrogates in well controlled sprays. A significant novelty with respect to previous work is the use of an electrospray to generate initially monodisperse droplet size distributions whose evaporation would be monitored in a preheated inert stream under laminar conditions. The fuel mixture consists of hexadecane ($C_{16}H_{34}$, 89.7 wt.%), naphthalene ($C_{10}H_8$, wt.9%), TMPD ($C_6H_8N_2$, *N,N,N',N'*-Tetramethyl-1,4-phenylendiamin, 1.0 wt.%), and an electrical conductivity enhancer Stadis 450. Such a mixture, although not a typical jet fuel surrogate, was chosen because it is widely used in the spray laser spectroscopy literature to distinguish the liquid phase from the vapor one. Vapor fluorescence centered at 400 nm is calibrated using a heated laminar coflow vapor jet diluted with nitrogen, and is found to be proportional to the vapor mole fraction up to 500 ppm. Vapor fluorescence is found to increase with temperature up to 538 K and then declines. Fluorescence from the liquid phase, i.e. the exciplex (Naphthalene+TMPD)*, is imaged at different fuel flow rates and ambient temperature. These measurements are correlated with complementary ones using a Phase Doppler Particle Analyzer to determine droplet size, velocity, number density and, ultimately, droplet evaporation rate along the spray axis. Additional complementary measurements using sampling of the fuel vapor and off-line gas chromatograph/mass spectrometry analysis to assess its composition are planned to have as well characterized a description of the spray environment and assess conclusively the potential of the exciplex approach for more challenging turbulent spray systems.

TECHNICAL DISCUSSION

Introduction

Spatially-resolved nonintrusive laser-based measurements of evaporating and combusting sprays are highly desirable for model development and combustor design, but represent a major technical challenge. Exciplex-PLIF is among the very few options capable of shedding information on both the vapor and liquid phases. The method is based on the reversible equilibrium between excited TMPD molecules and naphthalene, i.e. $TMPD^* + C_{10}H_8 \leftrightarrow (TMPD + C_{10}H_8)^*$ [1]. In the vapor phase, the naphthalene concentration is so low that exciplex formation can be neglected. Thus, upon excitation with a UV laser beam the

excited TMPD molecules directly release photons and return to the ground state. In the liquid phase, the naphthalene concentration is sufficiently high to convert almost all of the excited TMPD molecules to $(TMPD + C_{10}H_8)^*$. The exciplex then releases photons and returns to the ground state. Exciplex fluorescence has a longer wavelength than the vapor fluorescence because of the energy absorption in the formation of the exciplex. As a result, the fluorescence from the liquid phase can be spectroscopically discriminated from that of the vapor phase using suitable optical filters.

The goal of the present study is to assess if the exciplex-PLIF strategy can be used *quantitatively* in evaporating sprays. The report is organized as follows: after a description of the experimental set up, measurements of the exciplex fluorescence of an electrospray are presented, followed by a presentation of the vapor fluorescence data and their calibration. Next, we introduce PDPA measurements of the droplet size and velocity distributions to correlate them with the spectroscopic ones. Ultimately we plan on integrating these measurements with sampling of either the fuel vapor or the liquid droplets and off-line gas chromatograph/mass spectrometer analysis of the sample chemical composition. A comprehensive database will be assembled for a conclusive evaluation of the potential of the exciplex fluorescence for quantitative use in more challenging turbulent environments. The work to date was carried out by Dr. Tongxun Yi, a Postdoctoral Associate at Yale.

Experiment Set-up

Figure 1 shows the experimental setup. A monodisperse, dilute spray is generated using an electrospray atomizer. The latter consists of a stainless steel capillary tubing (ID 0.2 mm; OD 0.4mm) that, charged at a few thousand volts, disperses a conductive liquid into fine droplets. We operate the device in the so-called cone-jet mode [2], resulting in the generation of initially monodisperse droplets. To study their evaporative behavior, the spray is issued in a preheated stream of nitrogen. To prevent liquid boiling in the conical meniscus which would disrupt the electrospray dispersion, the temperature in the liquid line is independently controlled with a cooling nitrogen stream. The hypodermic tube is placed inside a Teflon tube (ID 1.6mm), that is positioned within a ceramic sheath tube (ID3.2mm; OD6.4mm) whose exit is capped by ceramic paste. The nitrogen is introduced into the Teflon tube, and exits through the gap between the Teflon tube and the ceramic sheath. The capillary at the center of the fuel injection system protrudes three millimeter above the outer coflow outlet. The outer coflow temperature is controlled using a CN9000 Omega controller. By varying the flow rate of the inner nitrogen stream, the temperature of the meniscus at the tip of the capillary tube can be independently controlled. With the present arrangement, the outer coflow hot stream can be operated up to 623 K without disrupting the electrospray dispersion. As a result, the system is well suited to study the evaporation of a laminar spray under well controlled conditions.

The fuel mixture consists of hexadecane ($C_{16}H_{34}$, 89.7 wt.%), naphthalene ($C_{10}H_8$, wt.9%), TMPD ($C_6H_8N_2$, *N,N,N',N'*-Tetramethyl-1,4-phenyldiamin, 1.0 wt.%), and traces of an electrical conductivity enhancer, Stadis 450. Such a mixture, although not a typical jet fuel surrogate, was chosen because it is widely used in the exciplex literature and there would have been not sufficient time and funding to investigate different exciplex candidate molecules to match the volatility of typical reference fuels in jet fuel surrogates.

Fluorescence from the exciplex, i.e. (Naphthalene+TMPD)*, is excited with the third harmonic of a Nd:YAG laser at 355 nm. To image the exciplex fluorescence, a Corion bandpass filter P10-490 with 490 nm center wavelength and FWHM 10 nm is placed in front of the PCO ICCD camera. When the vapor fluorescence is imaged, the P10-490 filter is replaced with the S25-400 filter. The bottom of the laser sheet is two mm above the Taylor cone. However, fluorescence from the Taylor cone can still be detected due to a laser reflection from a dye cell used for intensity calibration of the laser beam.

A TSI Phase Doppler Particle Analyzer (PDPA) is used to measure the droplet diameter and axial velocity. An Ar-ion laser beam (543.5nm) is split into two beams that are focused in a probe volume with the characteristic fringes from interference effects. The scattering signal of droplets traversing the probe volume relays velocity information through the signal frequency and size information from the phase difference between signals from strategically positioned photodetectors. The receiver is located at 30° in the forward direction. By moving the spray rig in

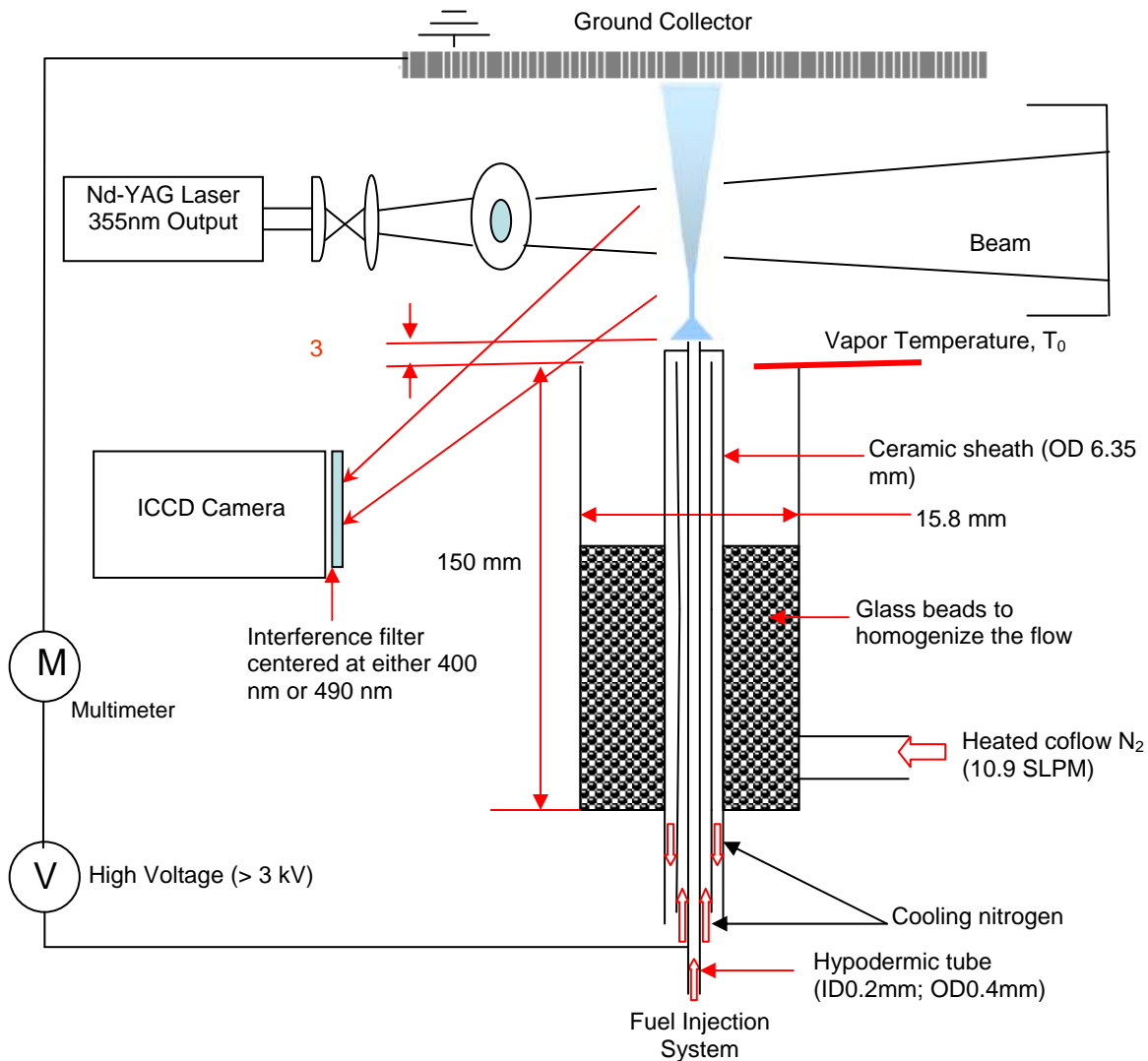


Figure 1. Spray rig and optical setup.

the horizontal and vertical directions, droplet and velocity distributions within the spray can be mapped out. Not shown in Fig.1 is a microscope system to monitor the morphology of the conical meniscus and the jet issuing from the cone apex during operation. A fine thermocouple was used to map the temperature field in which the spray was evaporating.

Exciplex Fluorescence

Figure 2 shows fluorescence from the exciplex, (naphthalene+TMPD)^{*}, as a marker of the liquid phase, at different coflow temperatures and fuel flow rates. The large bright spot at the bottom of each figure is the exciplex fluorescence excited by the laser reflection from the dye cell. The strongest fluorescence intensity is observed at 473 K because more TMPD is contained in each evaporating droplet having a relatively modest evaporation rate. The spray disperses radially outward downstream at 473 K at higher temperatures. This can also be explained by the droplet longer lifetime because of a lower evaporation rate. The radial dispersion is caused by Columbic repulsion of homopolarly charged droplets. Almost no exciplex fluorescence is discernible from Fig. 1(d) for a flow rate of 0.5 mL/hr and a coflow temperature of 573 K, probably because the droplets are too small to be detectable after having sustained sufficient evaporation in the hot stream before reaching the laser probe volume.

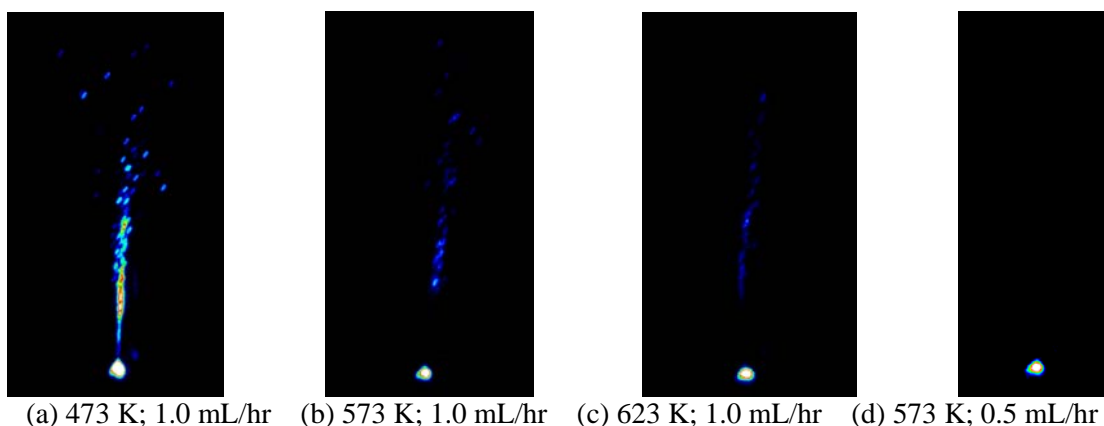


Figure 2. Exciplex fluorescence at different coflow temperature and flow rates. Each image is the average of 16 instantaneous snapshots. For comparison, the same intensity scale is used for all images.

Vapor Fluorescence

Figure 3 shows vapor fluorescence at different coflow temperatures. The liquid fuel flow rate is 0.5 mL/hr. The large bright spot at the bottom of each figure is vapor fluorescence from the immediate vapor layer around the conical meniscus. The strong signal suggests that evaporation from the Taylor cone may be a significant fraction of the total evaporated mass. From the morphology of the Taylor cone as observed through the microscope, one can estimate the residence time in the cone at about 1s at the flow rate of 1.0 mL/hr, by ratioing the cone volume and the volumetric flow rate. Clearly seen in Fig. 3 is the increase in vapor fluorescence with coflow temperature. First, at higher coflow temperatures a larger percentage of vapor is produced because of the higher evaporation rate; second, more vapor is concentrated along the axis because it takes a finite time for the droplets to diverge off the axis. Despite the fact that the fluorescence yield at 623 K is smaller than that at 523 K (see below), the fluorescence intensity

is still stronger, which obviously can be attributed to higher vapor concentration. At the coflow temperature of 473 K, individual droplets can be easily identified in Fig. 3(a), with the highest vapor concentration in the immediate layer around the droplets; at 523 K the vapor fluorescence is much stronger but individual droplets are still detectable; at 623 K the vapor fluorescence is so strong that individual droplets are barely detectable except at the spray boundary. The images in Fig. 3 are obtained by averaging 16 instantaneous snapshots. Figure 3 (a) suggests that the electrospray is indeed very dilute, with only a few droplets in a single 10 ns snapshot. The diluteness of the spray allows one to neglect laser extinction and secondary Mie-scattering. From figures 3(a-b), one can identify a bright column above which the droplets start to disperse radially outward due to Columbic repulsion. The width of vapor fluorescence is narrower at 623 K than at 523 and 473 K, which can be attributed to a higher evaporating rate and a shorter droplet lifetime.

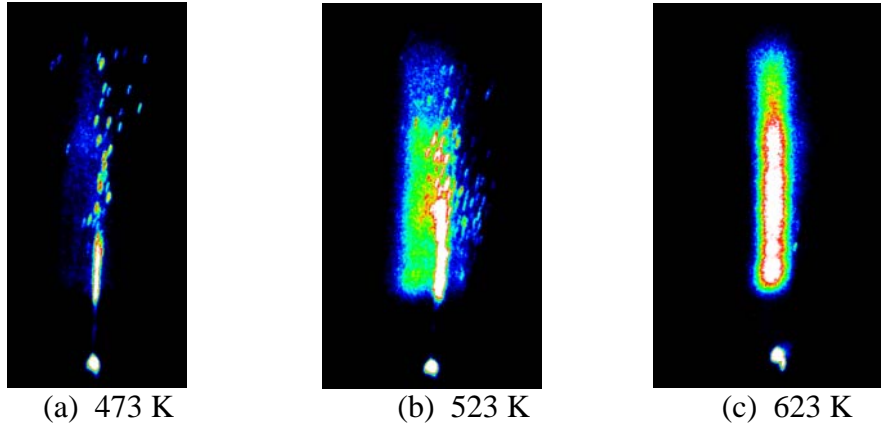


Figure 3. Vapor fluorescence at different coflow temperature. The fuel flow rate is fixed at 0.5 mL/Hr. Each image is the average of 16 instantaneous snapshots. For comparison, the same intensity scale is used for all images.

Figure 4 shows vapor fluorescence at different liquid fuel flow rates. The coflow temperature is fixed at 623 K. At the fuel flow rate of 0.5 mL/hr, droplets are barely visible; at 1.0 mL/hr only a few droplets are identifiable at the spray periphery; at 2.0 mL/hr, droplets appear both inside the spray and at the periphery. In fact, at the same coflow temperature, the droplet diameter increases

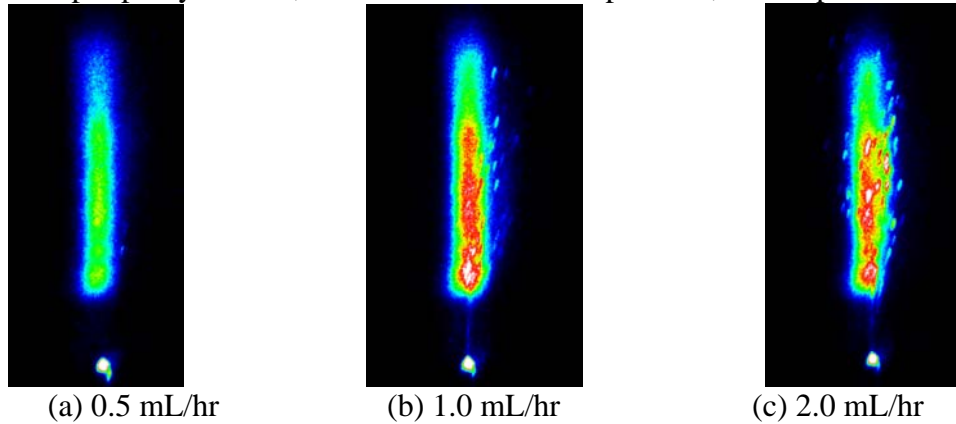


Figure 4. Vapor fluorescence at different fuel flow rates. The coflow temperature is fixed at 623 K. Each image is the average of 16 instantaneous snapshots. For comparison, the same intensity scale is used for all images.

with the fuel flow rate, and a larger droplet diameter implies a longer lifetime. The fluorescence intensity at 0.5 mL/hr is weaker than those at 1.0 and 2.0 mL/hr, which obviously can be attributed to lower vapor concentration.

Figure 5(a) shows fuel vapor fluorescence vs. fuel flow rates at different vapor temperatures, as obtained in a separate calibration system in which the liquid was fully vaporized before being issued in the hot inert coflow. Linearity between vapor fluorescence and the flow rate is well preserved, suggesting complete evaporation and vapor/nitrogen mixing at the vapor-jet exit. At the prevailing nitrogen flow rate of 332.6 SCCM, the TMPD vapor concentration is 52.7 ppm if the fuel flow rate is 1 mL/hr. Thus by amplifying the horizontal coordinate by a factor of 52.7, one obtains the molar fraction of TMPD vapor in ppm units. Figure 5(b) shows the vapor fluorescence vs. temperature at different fuel flow rates. The fluorescence yield increases monotonically with temperature up to 540 K and then declines. The same trend was observed by Kim and Ghandhi [3], with two significant differences: first, in the present study the peak occurs around 540 K, about 60 K lower than the value reported by those authors; second, we found a weaker dependence of the fluorescence yield on temperature.

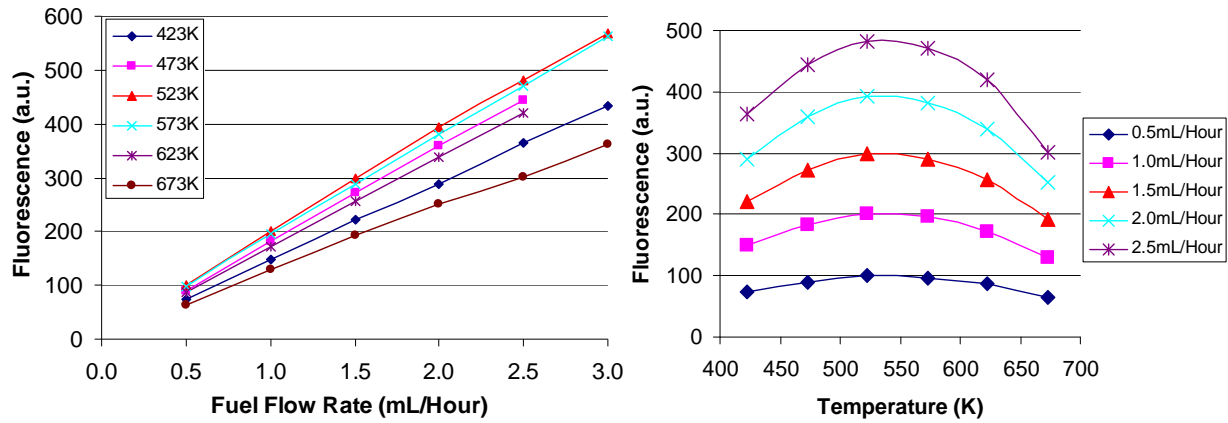


Figure 5. Fluorescence vs. (a) fuel flow rate and (b) vapor temperature temperature.

PDPA Measurements

Figure 6 shows histograms of the droplet diameter at different fuel flow rates. The droplet diameter increases with the fuel flow rate. No Columbic fission [4] occurs at flow rates below

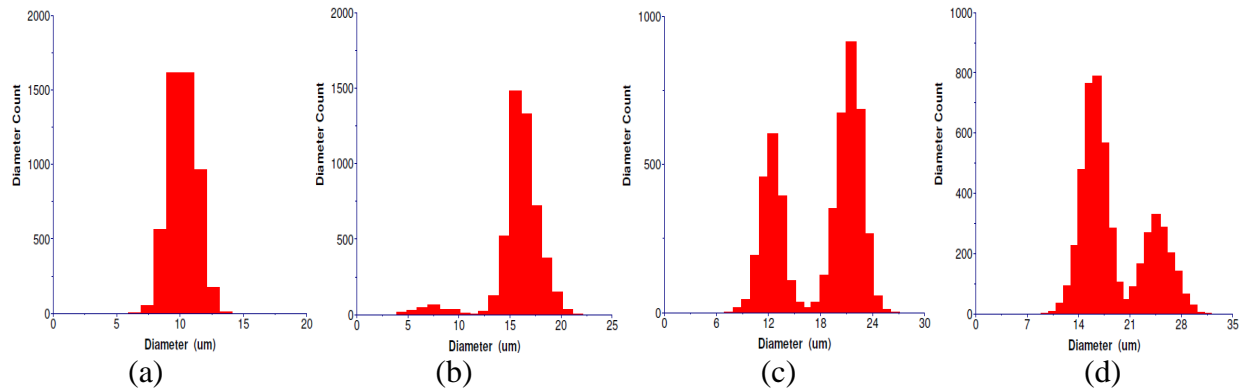


Figure 6. Histograms of droplets diameter. The voltage is 3059 V and the coflow temperature is 573 K. The measurement location is 4.4 mm above the tip of the capillary tube. Flow rate= 1.0 mL/hr (a); 2.0 mL/hr (b); 3.0 mL/hr (c); (d) mL/hr 4.0. The measurement location is 4.4 mm above the tube tip.

1.0 mL/hr and the spray is monodisperse. With increasing flow rates, more droplets undergo Columbic fission (see Fig.6(c)). At the flow rate of 4.0 mL/hr, the secondary droplets outnumber the primary ones.

Figure 7 shows the histogram of droplet diameter at three locations along the axis. Monodisperse droplets are generated at the flow rate of 1.25 mL/Hr and almost no Columbic fissions occurs. Thus the shrinkage in droplet diameter can be solely attributed to evaporation rather than the formation of offspring droplets. Monodispersity is gradually lost downstream along the axis and the diameter decreases because of the size-dependent evaporation rate (Fig. 7d). From Fig. 7(e), one can see that the mean droplet diameter decreases from 12.7 μm at $z=2.3$ mm to 6.5 μm at $z=15$ mm, i.e. the representative droplet has lost 87% of its initial mass.

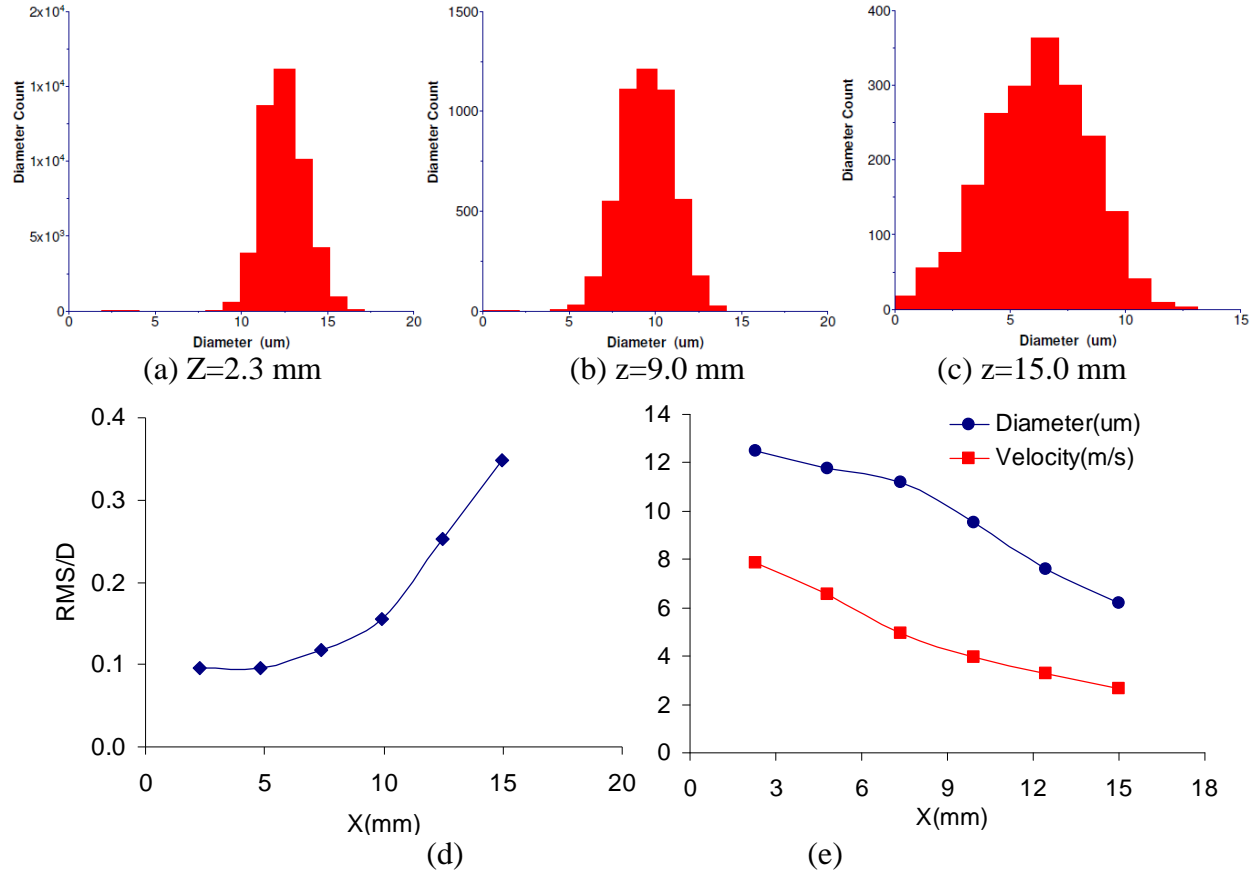


Figure 7. Histograms of droplet diameter at discrete locations along the spray axis. (a-c) Relative droplet standard deviation (d), mean diameter and velocity (e) along the spray axis. The flow rate is 1.25 mL/hr and the coflow temperature is 573 K.

The evaporating rate constant is determined from the PDPA measurements as

$$\frac{dD^2}{dt} = \frac{dD^2}{dx} \frac{dx}{dt} = 2V(x)D \frac{dD}{dx} = -K \quad (1)$$

After curve-fitting polynomials to the experimentally determined $D(x)$ and $V(x)$, the evaporation coefficient can be readily determined and is shown Fig. 8. The temperature variation along the axis is less than 20 K. Factors that can contribute to the observed trends and are presently being ascertained in more refined calculations include: the velocity slip between droplets and the host

gas that is more pronounced at the base of the spray and would increase evaporation rate; the increase in vapor concentration downstream that may decrease the concentration gradients driving the evaporation rate; and changes in the transport properties.

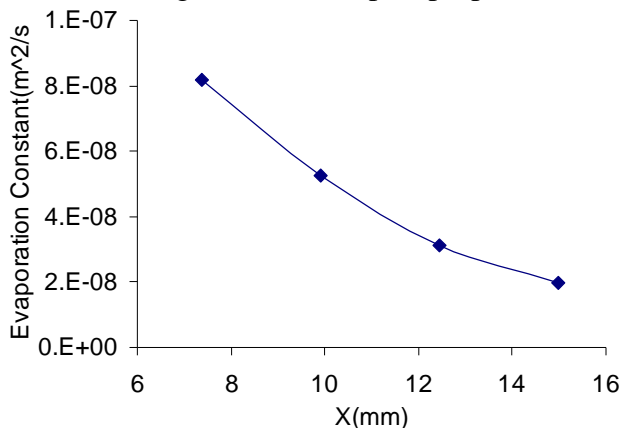


Figure 8. Evaporation rate constant along the spray axis. The flow rate is 1.25 mL/hr and the coflow temperature is 573 K.

Follow-up studies

Key objectives of the investigations were achieved, including: the establishment of a well controlled evaporating spray, setting up the exciplex-PLIF diagnostics and the complementary application of PDPA to measure droplet size, velocity and evaporation rate. Additional complementary measurements using vapor sampling and off-line gas chromatograph/mass spectrometry analysis are planned to have further redundancy in the database. At that stage, a refined data analysis will be applied using the governing equations to integrate/correlate the different diagnostic techniques. We anticipate a few additional months of activity, beyond the expiration of this short seed grant, to assess conclusively the potential of the exciplex approach for more challenging turbulent spray environments.

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